Effect of Electron-Electron Interaction on Transport in Dye-Sensitized Nanocrystalline TiO₂

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ABSTRACT

Experimental measurements and continuous-time random walk simulations on sensitized electrolyte-infused porous nanocrystalline TiO$_2$ films show that the actual electronic charge in the films is significantly larger than that estimated from small-perturbation methods by a constant, light-intensity-independent factor. This observation can be explained by small-perturbation techniques measuring the chemical diffusion coefficient of electrons instead of the normally assumed tracer diffusion coefficient of electrons. The difference between the two diffusion coefficients is attributed to the presence of an exponential density of states through which electrons interact. At high light intensities, an additional extra component owing to Coulomb interactions between the electrons is expected to arise.

1. Objectives

The photovoltage of the dye-sensitized solar cell is determined by accumulated electronic charge, presumably located in surface states or at grain boundaries in the TiO$_2$ nanocrystals [1]. The electronic charge accumulates because of the dynamic equilibrium between electron injection and recombination with the electrolyte. We have recently shown that the recombination process is transport limited such that the photovoltage of the cell is determined by electron transport [2]. An accurate measurement of the photoinjected charge is critical if we are to better understand the origin of the photovoltage, which will presumably lead to its optimization. This measurement has traditionally been done by small-amplitude modulation methods using the simple hypothesis that the charge equals the product of current and lifetime. Here, we show that, in the case of strong electron-electron interaction, this assumption is not necessarily true.

2. Technical Approach

2.1. Sample preparation and measurements

Dye-sensitized TiO$_2$ solar cells were prepared using standard methods [3]. The cells employed a transparent counter electrode. The cells were probed with a weak laser pulse at 690 nm (PTI nitrogen-pumped dye laser) superimposed on a relatively large, background (bias) illumination at 680 nm (0.5 W SDL model 7421 H1 laser diode). The probe light was incident from the counter-electrode side, and the bias light entered the cell from the collecting-electrode (substrate) side. The light intensity of the probe light was low to ensure negligible effect on the steady-state photocarrier density. The photoinduced electron density in the TiO$_2$ film was determined by charge-extraction measurements [4]. The bias-light source was the red diode laser mentioned above. The photoinduced charge in the film was determined by numerically integrating the photocurrent decay after the steady-state light was switched off.

2.2. Computer simulations

Electron-transport dynamics were modeled computationally using the continuous-time random-walk (CTRW) approach [4,5]. A three-dimensional grid of sites (typically 50x50x50 sites) representing traps was initialized by giving each site an energy drawn randomly from an exponential distribution:

$$g(\Delta E) = g_{tot} \frac{\alpha}{kT} \exp(-\alpha \frac{\Delta E}{kT}) \quad (1)$$

where g_{tot} is the total density of traps, α is the disorder parameter, $\bullet E$ is the energy difference between the conduction band-edge and the trap level (E_c-E_T), T is the absolute temperature, and k is the Boltzmann constant. The waiting time at the grid site was thermally activated

$$t_{em} = v^{-1} \exp\left(\frac{\Delta E}{kT}\right) \quad (2)$$

where v is the attempted-escape frequency from a trap. The parameter α is given by $\alpha = kT/m_c$, where m_c is the average depth of a trap in the exponential density of states. In the simulations, a large number of electrons was subjected to an exclusive random walk on the grid. In this fashion, current transients with or without a bias light could be simulated. From the simulations, chemical and tracer diffusion coefficients were determined.

2.3. Theory

The electron flux at any place in the film can be expressed as [3]

$$J_n = -D_n \underbrace{\left(\frac{\partial \overline{\mu}_n / kT}{\partial \ln n}\right)_{P,T}}_{\text{thermodynamic factor}} \nabla n = -D_{ch,n} \nabla n \quad (3)$$

where D_n is the tracer diffusion coefficient, related to the microscopic mobility by the Einstein relation: $D_n = (kT/q)m_n$ and defined by the well-known Einstein-Schmolukowski relation $D_n = <\bullet r^2>/6t$. The term in parentheses in Eq. 3 is the thermodynamic factor, T_n, which, in general, is equal to one, but, in the case of interaction between diffusing particles, can potentially differ from one.

For the case of an exponential distribution of states and assuming Fermi-Dirac statistics, the following relationship for the thermodynamic factor T_n is obtained:

$$T_n = \left(\frac{\partial \overline{\mu}_n / kT}{\partial \ln n}\right) = \frac{1}{\alpha} + \frac{q^2 n}{kTc_H} \cdot \quad (4)$$

The thermodynamic factor is predicted to be a constant ranging between 2 and 10 [2], independent of light intensity. Note that at high light intensities, this factor is strongly light-intensity dependent, with the turnover point occurring at ca. 1 sun.

3. Results and Accomplishments

Figure 1 shows results of experimental measurements on dye cells by two methods. The parallel slopes indicate that the photoinjected charge in the film is a constant factor higher than that estimated from small-perturbation techniques independent of light intensity.
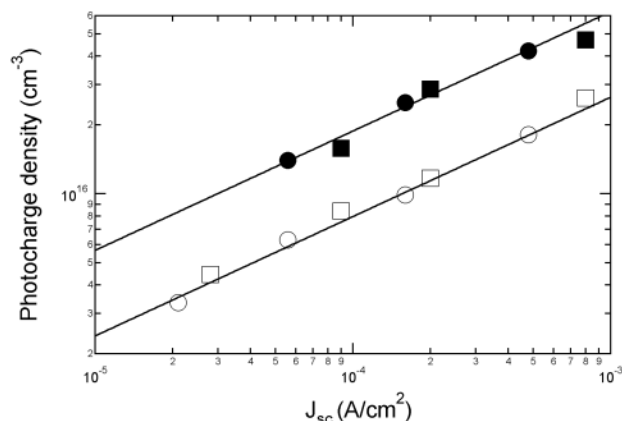

Fig. 1. Results from charge-extraction measurements (closed symbols) and small-perturbation techniques (open symbols). The continuous lines are power-law fits.
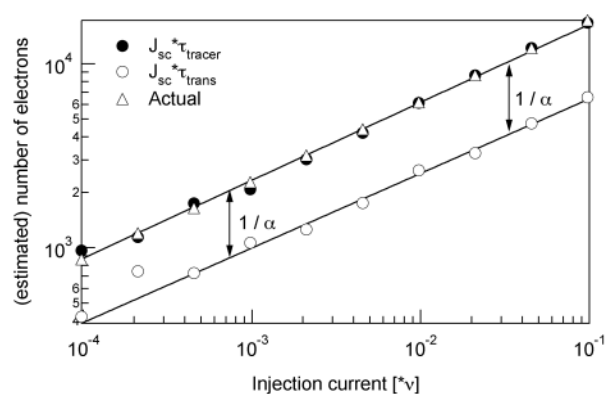

Fig. 2. CTRW simulations of electron transport in the dye cell. The filled circles indicate charge estimated from the tracer diffusion coefficient, and the open circles indicate charge estimated from the chemical diffusion coefficient. The open triangles indicate the actual charge in the film. The continuous lines are power-law fits.

The same effect is observed in the CTRW simulations as in the experimental measurements: the charge is a constant factor higher than that estimated from photocurrent transients (Fig. 2). The constant factor is precisely $1/\alpha$, consistent with the theoretical result (Sec. 2.3). It is also shown that when the charge is estimated from the tracer diffusion coefficient instead of the chemical one (obtained from the photocurrent transient), the charge does correspond to the real charge. This result indicates that the photoaccumulated charge in the film is determined by the tracer diffusion of electrons. Also, since in these cells the electron lifetime is inversely proportional to the (tracer) diffusion coefficient of electrons, the same effect applies to open-circuit conditions. Note that at high light intensities, a deviation from the constant difference between the two diffusion coefficients is expected due to a higher number of photoaccumulated charges than the current generation.

4. Conclusions

It is shown that the actual photoaccumulated charge in dye-sensitized TiO_2 solar cells is considerably higher than that estimated from small-perturbation methods. The difference is caused by strong electron-electron interaction mediated by an exponential density of states. It is predicted that for future high-efficiency solar cells, Coulomb interaction between electrons will begin to play a major role.

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